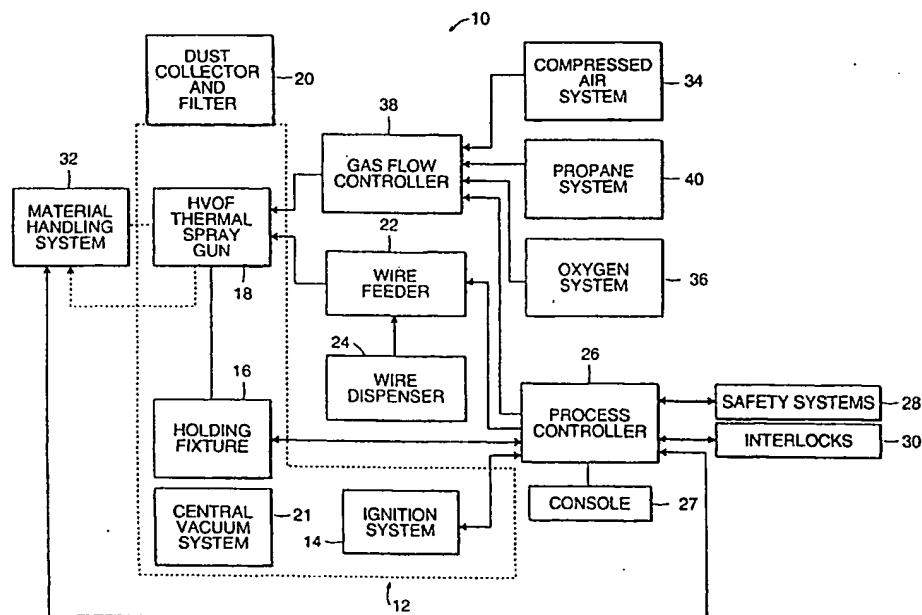




## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>7</sup> : <b>C23C 4/12</b>		<b>A2</b>	(11) International Publication Number: <b>WO 00/29635</b>
			(43) International Publication Date: 25 May 2000 (25.05.00)
(21) International Application Number: <b>PCT/US99/26634</b>		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).	
(22) International Filing Date: 12 November 1999 (12.11.99)			
(30) Priority Data: 60/108,223 13 November 1998 (13.11.98) US 60/162,577 29 October 1999 (29.10.99) US			
(71) Applicant (for all designated States except US): THERMOCE- RAMIX, L.L.C. [US/US]; 101 Federal Street, Boston, MA 02110 (US).			
(72) Inventors; and (75) Inventors/Applicants (for US only): ABBOTT, Richard, C. [US/US]; 68 Old Colonial Drive, Gardner, MA 01440 (US). COLLIER, Paul, S. [US/US]; 13 Pond Path, North Hampton, NH 03862 (US). GLENN, William, A. [US/US]; 107 Broadmeadow Road, Groton, MA 01450 (US).		Published Without international search report and to be republished upon receipt of that report.	
(74) Agents: HOOVER, Thomas, O. et al.; Hamilton, Brook, Smith & Reynolds, P.C., Two Militia Drive, Lexington, MA 02421 (US).			

(54) Title: SYSTEM AND METHOD FOR APPLYING A METAL LAYER TO A SUBSTRATE



## (57) Abstract

The present invention relates to systems and methods for applying metal shielding coatings on substrates. More particularly, EMI/RFI shielding coatings are applied using an HVOF thermal sprayer adapted to increase the velocity of the molten metal particles. The shielding coatings have an adhesion characteristic and electrical conductivity level that is an improvement over the prior art shielding coatings.

*FOR THE PURPOSES OF INFORMATION ONLY*

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav	TM	Turkmenistan
BF	Burkina Faso	GR	Greece		Republic of Macedonia	TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's	NZ	New Zealand		
CM	Cameroon		Republic of Korea	PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakhstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

## SYSTEM AND METHOD FOR APPLYING A METAL LAYER TO A SUBSTRATE

### RELATED APPLICATIONS

This application claims the benefit of U.S. Provisional Application No.  
5 60/162,577 filed October 29, 1999 and U.S. Provisional Application No. 60/108,223  
filed November 13, 1998, the entire teachings of both of these applications being  
incorporated herein by reference.

### BACKGROUND OF THE INVENTION

10 Stray signals of Electromagnetic Interference (EMI) and Radio Frequency  
Interference (RFI) generated by static sparks or outside signals can effect many  
types of sensitive and critical electronic equipment such as computers, medical  
equipment, navigational instruments, communication systems and process controls.  
Electrically conductive coatings are typically used for shielding from RFI or more  
15 generally EMI. These electrically conductive coatings are often necessary to shield  
electronic devices that are contained in enclosures that are not themselves  
electrically conducting such as an enclosure made from plastics or ceramics.

EMI/RFI shielding is based on the general laws of electromagnetism which  
state that the electric field due to an external source inside a fully enclosed electrical  
20 conductor is zero. Thus, an enclosure, such as a plastic housing for an electronic  
device which is coated with an electrically conductive coating such as a metallic  
layer will protect the device from outside electromagnetic interference. Conversely,  
an electronic

- 2 -

device which emits electromagnetic radiation will be fully shielded by such an enclosure so that the electromagnetic field due to the device is zero outside.

There are numerous ways to shield an electronic device. They include using an inherently conductive enclosure such as a metal or an electrically conductive  
5 element applied to a nonconducting enclosure such as adhesive foils, thin metal sheets or conductive gasket materials. Conductive coatings can be applied to the enclosure by paint, evaporative metals, sputtered metals or thermal spray.

In the thermal spray technique, an arc wire spray device is typically used to deposit a coating of zinc, copper, aluminum, or other metal to the surface of the  
10 enclosure. The arc wire spray apparatus functions by melting the tips of two wires, usually zinc, and transporting the resulting molten droplets by means of a carrier gas to the surface to be coated. When the droplets impact the surface, they rapidly solidify to form a coating. The coating is built up by multiple traverses of the spray apparatus over the coated surface. The wires or feedstock are melted by an electric  
15 arc generated by a potential difference between them. The carrier gas is typically compressed air.

In another thermal spray technique, a flame spray apparatus is used where the feedstock, which can be a wire or a powder, is melted by means of a combustion flame. The combustion is usually effected through ignition of gas mixtures of  
20 oxygen and another gas such as acetylene.

Both thermal spray techniques can be used to apply EMI/RFI shielding coatings, however, the coatings are not fully dense so that electrical conductivity is diminished and the deposited surface has a rough appearance. Moreover, the substrate must be prepared for coating by roughening so that the coating bond  
25 strength is enhanced. This preparation step is often a grit blasting operation or application of a primary coating. Finally, the arc wire sprayed coating contains residual tensile stresses that tend to delaminate the coating from the substrate, especially at the edges.

- 3 -

## SUMMARY OF THE INVENTION

The present invention relates to systems and methods which include a high velocity thermal spray apparatus to apply metals, such as EMI/RFI shielding coatings for example, to substrates. The present invention is predicated on the  
5 recognition that most of the disadvantages of the prior art arc wire and flame spray techniques, arise from the fact that the speed of the molten droplets is too low. The present invention recognizes that increasing the speed of the molten droplets to about 330 to 1000 meters/second greatly improves upon various limitations of the prior art methods.

10 A preferred embodiment of the present invention uses a high velocity oxy-fuel (HVOF) thermal spray apparatus to apply EMI/RFI shielding coatings onto substrates. An HVOF apparatus uses combustion gases, such as propane and oxygen, that are ignited in a small chamber. The high combustion temperatures in the chamber cause a concurrent rise in gas pressure which in turn, generate a very  
15 high speed effluent of gas from an orifice in the chamber. This hot, high speed gas is used to both melt a feedstock, for example, wire rods, and transport the molten droplets to the surface of the substrate at speeds in the range of about 330 to 1000 m/sec. Compressed gas such as for example, compressed air is used to further accelerate the droplets and cool the HVOF apparatus. The feedstock may be either  
20 wire or powder.

When the molten droplets impact the substrate their speed is high enough that the coating density approaches one hundred percent of the maximum theoretical density. The coating density is preferably in a range between 95% and 100% of the theoretical density. This greatly improves electrical conductivity and coating bond  
25 strength. Moreover, there is frequently a compressive stress in the deposited material which reduces the tendency to delaminate and improves the bond strength.

In a preferred embodiment, the initial step of roughening or preparing the substrate prior to the application of coatings, can be eliminated using the system and apparatus of the present invention because bond strengths are at an adequate level.

- 4 -

In an alternate preferred embodiment, the plastic housing can be pre-roughened using a fine grit or a primary coat.

In a preferred embodiment, the high velocity oxy-fuel thermal spray apparatus includes an HVOF thermal spray gun in which air-under pressure is used to accelerate the molten metal droplets. The nozzle assembly of the HVOF thermal spray gun is adapted to accelerate the molten metal particles to supersonic velocities in a range between about 330 m/sec and 1000 m/sec for example, by introducing air under pressure in the air cap region at the exit of the nozzle assembly.

One exemplary use of the system and method to apply EMI/RFI shielding coatings is to shield plastic wireless phone housings and the internal electrical components from EMI/RFI. In a preferred embodiment, the method to apply EMI/RFI shielding coatings includes the step of masking the plastic wireless phone housing. The masked material is made from either machined metal, molded rubber compound or other plastic. Once the material handling process of the substrate, for example the masking process is complete, the method includes the step of feeding the HVOF thermal spray system with metal feed stock, for example, a zinc wire having a diameter ranging from about 0.0625 to 0.125 inch and melting the wire using combustible fuels, such as propane, and oxygen. The method includes the step of cooling the spray apparatus with compressed air. The compressed air also augments the velocity of the molten metal. The method includes the step of depositing metallic coatings on the surface of a substrate. In a preferred embodiment, a plastic housing is coated to a thickness of about 0.002 inches of zinc. The resultant electrical resistance over a three inch section is less than 0.1 ohm with a bond strength that is greater than required of a tape peel test.

The adhesion characteristic of the HVOF sprayed coatings in accordance with the present invention are in the range of about 650 to 1070 psi. The electrical conductivity of the coatings in accordance with the present invention is in the range of about 5 to 10 mohms/square cm.

The foregoing and other objects, features and advantages of the system and method for applying EMI/RFI shielding coatings will be apparent from the

- 5 -

following more particular description of preferred embodiments of the system and method as illustrated in the accompanying drawings in which like reference characters refer to the same parts throughout the different views. The drawings are not necessarily to scale, emphasis instead being placed upon illustrating the

5 principles of the invention.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a block diagram illustrating the system for applying EMI/RFI shielding coatings in accordance with the present invention.

Figure 2 is a schematic view illustrating the spray delivery system in

10 accordance with the system for applying EMI/RFI shielding coatings of the present invention.

Figure 3A is a side view of a HVOF thermal sprayer used in the spray system in accordance with the present invention.

Figure 3B is an exploded view of the HVOF thermal sprayer used in the

15 spray delivery system in accordance with the present invention.

Figure 4 is a cross-sectional view of a preferred embodiment of the nozzle assembly of the HVOF thermal sprayer.

Figures 5A - 5G are cross-sectional and end views of different preferred embodiments of the nozzle assembly used with the HVOF thermal sprayer in

20 accordance with the present invention.

Figure 6 is a view of a mixing plug used in the HVOF thermal sprayer in accordance with the present invention.

Figures 7A and 7B are a views illustrating a preferred embodiment of the HVOF thermal sprayer in accordance with the present invention.

Figure 8 is a view illustrating a preferred embodiment of the robot used in

25 the system for spraying EMI/RFI shielding coatings.

Figure 9 is a view illustrating a preferred embodiment of a material handling system of the system for spraying EMI/RFI shielding coatings onto surfaces of substrates.

- 6 -

Figure 10 is a view of the inside of a back cover of a wireless telephone that has been sprayed with EMI/RFI shielding coatings in accordance with the present invention.

Figure 11 is an exploded view of a wireless telephone having EMI/RFI shielding coatings applied using the system and method of the present invention.

Figure 12 is a flowchart illustrating the method for applying EMI/RFI shielding coatings to substrates using the present invention.

#### DETAILED DESCRIPTION OF THE INVENTION

10 The present invention is directed to systems and methods for applying metals onto substrates, including for example, the application of EMI/RFI shielding to various substrates.

Referring to the figures, Figure 1 is a block diagram of the system 10 used for applying EMI/RFI shielding coatings in accordance with the present invention.

15 In a preferred embodiment, the system includes a fully enclosed acoustic spray booth 12 which contains an ignition system 14, a holding fixture 16 and a high velocity oxy-fuel sprayer or spray gun 18. The system further includes a dust collector and filter system 20 which includes a downdraft table, an air management module with spark trap, a downflow dust collector and a fan to support the dust collector. A high efficiency particulate assembly (HEPA) filtration unit, and a central vacuum system is included in the dust collector and filter system 20 of the present invention. A wire feeder 22 with closed loop electronic system and a wire dispenser 24 are also included in the system of the present invention. A process controller 26 that interfaces with a safety system 28, interlocks 30 and a material handling system 32 is included in the system 10.

In addition, a compressed air system 34 with water and oil separators and dew point monitoring are included in the system 10 for applying EMI/RFI shielding coatings of the present invention. A bulk oxygen supply system 36 including plumbing from the bulk source to a gas flow controller 38 is included in the system 10. A bulk propane supply 40 with appropriate plumbing is also included to supply

- 7 -

propane from the bulk source to the gas flow controller 38. The gas flow controller controls the mass flow of oxygen, propane and of compressed air into the HVOF spray gun 18. A mask system, and a mask washer system which are included in the material handling system 32 also form part of the system for applying EMI/RFI

5 shielding coatings.

The process equipment includes a holding fixture 16 for the HVOF thermal spray gun such as for example, a six-axis robot similar to a welding system with horizontal and vertical travel adequate for a designed material handling system, for example, Fanuc S500 manufactured by Fanuc Robotics Corporation. The robot is

10 fitted with a wire feeder, breakaway end effector, and bracket to support the thermal spray gun 18. The robot has a secure pedestal. The minimum payload of the robot is approximately 10 kg. The robot has a minimum horizontal travel rate of 1000 mm/sec, minimum path repeatability of 0.010" and a high speed option on the sixth axis. The robot is protected from high ambient dust levels. In another preferred

15 embodiment, the holding fixture 16 can be stationary or move in one plane for example, the xy plane.

The system has a remote operator control station for example, the process controller 26, with a computer readable medium drive such as a floppy disc drive, extended data memory storage, CRT/keyboard and cables. The controller 26

20 provides mechanical, electrical and software interface for operation of the HVOF thermal spray gun 18, safety systems 28, interlocks 30, and material handling 32 and a spray booth 12. Safety systems 28 include, but are not limited to, gas leak detector, and sensors for safe operation. Interlocks 30, include, but are not limited to mechanisms and devices to provide for accurate and safe operation of the hardware.

25 The fully enclosed acoustic spray booth 12 meets all federal, state and local codes for fire, health and safety. The spray booth 12 contains windows suitable for visual observation of the bulk of the material handling and spray equipment. The booth access doors contain safety interlocks capable of shutting down all machine and process functions, if opened. Personnel are alerted with flashing lights and

30 audio alarm if a fault is detected. A computer displays location and disposition of

- 8 -

system fault or failure. All control and software equipment supports safety interlock violations in the same manner as standard safety lock out and tag out procedures.

All lighting used inside the booth 12 meets all codes, federal state and local pertaining to vision standards, and all applicable safety standards per this process.

- 5 The booth 12 is sized in such a manner as to accommodate all material handling equipment, all spray equipment, all health, safety and fire suppression equipment. The booth is adequately designed to accommodate maintenance issues, with an emphasis on routine tasks. The booth surfaces, inside and outside, are cleaned routinely with common commercial cleaners. The construction of the booth
- 10 accommodates all structural issues associated with the modification of same, for any and all consideration unique to the process of the present invention, especially those for dust collection, cooling, sound and any others especially those affecting make up air supply. The booth 12 is equipped with the appropriate sensors to monitor the environment. A go/no go status is recognized by process control software for an
- 15 additional safety inter-lock system. Sensors are included for oxygen, propane, carbon, monoxide and any others to meet federal, state and local codes.

- A down draft table is located inside the spray booth 12. The booth is designed in such a manner that it maintains a flow of 125 CFM/sq.ft. face area. The down draft tables support equipment provides a flow rate of 3000 CFM over the
- 20 entire work surface.

- An air management module separates the largest metal particles. The particles are separated and collected at the air management module. The module employs a spark trap to ensure safe material collection and eliminates any explosive potential associated with metal powder and particulate collection. The air
- 25 management module is connected to a down flow dust collection unit where fine particles are separated and collected.

- A dust collection system 20 of a down flow type with an air management module promotes large particle drop out. Down flow systems are capable of efficiencies of 99.999% on sub-micron size particulate and are capable of collection
- 30 of large amounts of material for efficient storage and handling of collected waste

- 9 -

materials. This system is supported by a fan for transfer to a HEPA filtration system.

A fan is sized to support the dust collection system 20 via the down flow system along with the additional needs of the HEPA filtration system. All are  
5 monitored with a system control panel. This panel contains features needed for a complete and safe operation of the system.

A HEPA filtration unit is a part of the total dust collection system 20. It is the final air filtration portion of the dust collection system 20 and is supported by the air management module, the down flow system and the remote fan. This  
10 arrangement supports the vacuum system for the maintenance and cleaning of the spray booth 12 and its internal equipment.

A central vacuum system 21 is used to support the maintenance of the spray booth, down draft table along with the material handling equipment and other support equipment in the spray booth. This system is supported by the total dust  
15 collection system 20.

The spray gun ignition system 14 ignites the fuel gases at the HVOF thermal spray gun nozzle to initiate operation of the gun 18. It is mounted in a convenient place for the robot 16 to move to whenever the gun requires ignition. The ignition system 14 is, but not limited to, a carbide (resistance heater) type or a piezoelectric  
20 (spark) type and is controlled by the process controller 26. There is mounted a sensor, either blue/yellow flame detector, temperature sensor, or ignitor resistance sensor to provide feedback to the process controller 26 as to whether the fuel has been ignited.

An HVOF thermal sprayer 18 capable of efficiently depositing molten metal,  
25 for example zinc, at velocities in excess of about 330 m/sec up to about 1000 m/sec uses oxygen and propane as fuel gases and compressed air as a cooling and accelerating medium. The sprayer is fitted with a thermocouple or other temperature sensors located at the nozzle to detect operating conditions. The HVOF thermal sprayer 18 has appropriate hardware for mounting to the robot 16. Further, the  
30 sprayer 18 has flash arresters in its fuel gas lines mounted at the point of entrance to

- 10 -

the sprayer. Typical gas consumption rates for the sprayer are as follows:  
propane:25-45scfh, oxygen:225-325scfh, and compressed air:18-28scfm. In a  
preferred embodiment, zinc wire consumption rate ranges from 3 to 24 lb/hr and is  
preferably about 8.9 lb/hr.

5           The control console 27 interfaces with the process controller 26 and provides  
access to all controllable parameters including, but not limited to, the mass flow  
controllers, and metal feed. Mass flow controllers for oxygen, propane and air  
ensure the precise control and supply of gas to the process and are also connected to  
the interlock systems 30 to ensure process integrity. The wire feed system 22 is  
10       controlled for feed rate and monitored by the programmable controller 26. The wire  
feed is connected to the interlock system 30. Sensors, such as thermocouples,  
mounted on the sprayer 18 sense to ensure gas ignition and the maintenance of  
ignition. Any single violation of a sensed system engages the interlock system 30.  
Any process condition not in compliance with the process controller 26 is displayed  
15       on the main control screen of the control console 27 as a default condition,  
prompting corrective action.

          The wire feeder 22 and wire dispenser 24 form part of the system 10 for  
applying EMI/RFI shielding coatings to substrates. The wire feedstock includes,  
but is not limited to zinc, copper and aluminum and alloys thereof. In a preferred  
20       embodiment, the wire feedstock is received from a supplier in containers, for  
example, 500 lb drums of 1/8" zinc wire measuring 31"h x 20"diameter. A bulk  
wire dispenser is attached to the top of the drum and the wire is fed via a conduit 40  
leading into the spray booth 12 to a wire feeder 22. The wire feeder 22 is of a  
standard welding style capable of feeding, for example, 1/8" diameter wire at a  
25       minimum rate of 67 in/min. The feeder is controlled by the process controller 26 via  
an analog signal and indicates through feedback a non-feed condition. The wire  
feeder 22 of the present invention system 10 has a precise level of control over the  
feed rate as compared to prior art feeders. The precise control gives a more uniform  
spray rate and tighter coating thickness control. The process to coat substrate  
30       surfaces with EMI/RFI shielding coatings is thus more reproducible. Further,

- 11 -

power in the wire feeder 22 is sized for larger spools of wire and ranges from about 1/4 to 1 horse power.

The compressed air supply system 34 is sized and configured for continuous operation. The air compressor contains an air dryer and an oil and water separation system including inline filtration coupled with an electronic system that automatically monitors and controls the compressor operation. The system 34 has a microprocessor that interprets data from sensors placed in key locations in the compressor and optimizes operations based on preprogrammed parameters for maximum efficiency and reliability.

10 The bulk liquified oxygen and propane supply systems 36, 40 are located outside of the facility. All construction considerations, code compliance issues for federal, state and local agencies.

Mass flow controllers 38 or flow controllers for oxygen, propane and air are used in the system 10 in accordance with the present invention as they are a direct and absolute measuring device. They readily interface with computer controlled processes and ensure gas flow meter accuracy to about +/- 1%.

The mass flow controllers provide an improved control over gas flow rates, particularly feedback control, giving better flame temperature control and less flame turbulence. This allows for more uniform wire melting in the HVOF thermal spray gun 18. The flow rates can be controlled with electrical control signals inputted at the control console 27 to the programmable controller 26. Further, the gas flow rates may be reduced for ignition, then ramped up for normal operation, thereby eliminating the need for two-position valves for light-up.

Software is required to support all aspects of the process. This includes, but is not limited to, operation and motion of the robot, control of gas flows, wire feeder, ignition system, sensors, interlocks, booth operation, material handling, statistical process control and safety systems. Motion control software such as, for example, Fanuc thermal spray modules are used.

Gas Pressures (Typical operating)

30 Propane 60-90psi

- 12 -

Oxygen	60-90psi
Compressed Air	80-200psi

Flow Rates (Typical operating)

5	Propane	25-45scfh
	Oxygen	225-325scfh
	Compressed Air	18-28scfm

Spray Distance

10	4-12 inches (gun to part)
----	---------------------------

Traverse Rate (typical)

200-1200 mm/sec

15 Wire feed rate

3-24 lb/hr (zinc)

Wire diameters (inches)

1/16 – 1 /4 inches

20 Referring to Figures 2 and 3A, the HVOF thermal sprayer 18 used to spray the EMI/RFI shielding coatings onto surfaces of substrates is illustrated. The wire feeder system 22 including the wire dispenser 24 feed the wire feedstock to the sprayer 18. Gas flow controllers 38 provide mass flow of compressed air, propane and oxygen to the HVOF sprayer 18.

25 A wire conduit 40 supplies wire to the sprayer 18. In a preferred embodiment, a push wire feed system is used. The push principle permits a light weight sprayer without any moving parts or delicate systems. Additionally, the push principle allows the installation of the feeder outside the spray booth 12. In the alternative, a pull type wire feed system can also be used. Although the HVOF

- 13 -

thermal sprayer is illustrated as having a wire feed system, the HVOF thermal sprayer 18 can also be used with powder as feed stock. The powder can include metallic powders such as copper, aluminum, and composites containing an electrically conducting component and a plastic component for adhesion.

5           The HVOF thermal sprayer 18 is air-cooled and requires no water cooling. In a preferred embodiment, since the wire is pushed to the nozzle by the wire drive 42, the nozzle or sprayer has no moving parts and requires minimum maintenance. The process controller 26 remotely actuates the wire feed to a predetermined rate. The gas head provides efficient combustion, rapid melting of the wire and  
10 acceleration of the molten droplets to very high velocities (about 330 m/sec to 1000 m/sec). The gun is adapted for robot mounted operation with a mounting adapter 45 as shown in Figure 3A.

Fuel is delivered through a fuel supply line 44 to the gun 18. An oxygen supply line 46 supplies oxygen from the bulk oxygen supply to the gun. A  
15 compressed air supply line 48 supplies the air under pressure to the gun 18. The wire feedstock is supplied through the conduit 40 to the spray gun. The HVOF thermal spray gun body 47 includes a nozzle assembly 49.

Referring to Figure 3B, an exploded view of the HVOF thermal spray gun 18 is illustrated. The HVOF thermal spray gun 18 includes the nozzle assembly 49  
20 which includes an air cap body 50, an aircap 52 including an air cap 52a which produces a fan-shaped spray or an air cap 52b which produces a column-shaped spray. Further, the nozzle assembly 49 includes a nozzle nut 54, a nozzle 56 and a mixing plug 58. Though only illustrated with two air caps, a variety of air caps are provided for wire feed stock ranging from 1/16 inches to 1/4 inches diameter of  
25 wires to produce sprays with different shapes and patterns.

Referring to Figure 4, a cross-sectional view of the HVOF spray gun in particular, the nozzle assembly 49 is illustrated. Oxygen is introduced into the mixing plug 58 at groove 62. The fuel, for example, propane is introduced into groove 64 of the mixing plug 58. The oxygen and fuel gases are mixed in the body  
30 of the mixing plug 58 and flow downstream into the nozzle 56. The oxy-fuel

- 14 -

mixture enters the air cap 52. The air cap 52 has a nozzle restriction 66 or throat which confines the oxy-fuel flow to a smaller diameter core through the center of the nozzle bore 68. The wire feedstock is introduced into the nozzle bore 68 in the body 47. The restriction increases the velocity of the oxy-fuel mixture. Air at a high  
5 pressure ranging from 80-200 psi is introduced into the air cap 52 at groove 70. Compressed air is used prior to its introduction into the air cap 52 to conductively cool the nozzle assembly 49 by flowing along the surfaces of the nozzle assembly. Once introduced into the air cap 52, the compressed air accelerates the oxy-fuel mixture and the molten metal droplets to speeds ranging from 330 m/sec to 1000  
10 m/sec.

Figures 5A - 5G are cross-sectional and end views of different preferred embodiments of air caps used with the HVOF thermal spray gun 18 in accordance with the present invention. Referring to Figure 5A, an air cap 100 of a preferred embodiment of the HVOF thermal spray gun 18 is illustrated. The air cap 100 has  
15 two air ports 102, 104 as seen in the end view illustrated in Figure 5B. Compressed air enters the spray gun at groove 70 and flows downstream in the air channel 106. The air accelerates the molten metal droplets at the exit of the air cap. The spray pattern that is formed using this air cap 100 approximates a fan-shape.

Figures 5C and 5D illustrate an alternate, preferred embodiment of an air cap  
20 110 in accordance with the present invention. The air ports are increased in this particular embodiment and can range from 2 to 12 air ports. Further, an air inlet 114 is provided which supplies air from an air amplifier which increases inlet air pressure to a range of about 125 to 200 psi. This higher pressure effectively accelerates the speed of the molten metal droplets to above Mach 1. This air supply  
25 into the air cap has separate controls than the HVOF thermal spray gun 18.

Referring to Figure 5E - 5G, the air cap 128 has a portion of the front end 130 modified by installing a 0.312 radius bore 129 at the center of the center bore 132 of the air cap 128. This preferred embodiment of the air cap 128 allows the metal spray stream to be sprayed at close to 90° angles relative to the gun tip. An  
30 additional hole 136 is installed in the air feed system. This allows for the spraying

- 15 -

of internal bores, as well as difficult geometries containing obtuse or inverse angles, that are perpendicular to the air cap.

Referring to Figure 6 a view of a mixing plug 58 used in a preferred embodiment of the HVOF thermal spray gun 18 in accordance with the present invention is illustrated. The mixing plug includes a flange 140, grooves 142, 144 and gaskets 146, 148, 150. Gases such as, for example, oxygen and fuel gases are fed into the inner bore 132 after being introduced at different points. The fuel gases, such as propane is introduced into the groove 142 and oxygen is introduced into the groove 144. The oxygen and fuel gases mix in the inner bore 132.

Figures 7A and 7B are views illustrating a preferred embodiment of the HVOF thermal spray gun 18 in accordance with the present invention. A gas tight seal between the mixing plug 58 and the nozzle 56 is disposed. Figure 7B shows the two gaskets 62, 64 which provide improved sealing. The two gaskets perform separate as well as complimentary functions. The inner gasket 62 insures sealing between the wire feed system 22 from the central bore 132 eliminating the potential for flashbacks due to gas buildup. The outer gasket 64 insures the elimination of gas in the gun housing and the tight seal promotes stable gas mixing and pressures within the nozzle 56.

Figure 8 is a view illustrating a preferred embodiment of a robot 160 in accordance with the present invention. The six-axis robot has a streamlined and lightweight mechanical configuration and a large work envelope. It is ideal for medium size, low-cost, high speed operations. It utilizes digital servo drives and alternating current (AC) servo motors with absolute positioning for high performance and reliability. The robot 160 provides the following features and benefits:

- $\pm 0.1$  mm ( $\pm 0.004$ ") repeatability
- 1529mm (60.2") maximum reach
- High speed/multiple turn wrist axes
- 300° base rotation
- AC servo digital drives, absolute encoder positioning, rotary vector (RV) speed reducers and harmonic drives.
- Can be mounted on the floor, on an angle or in an inverted configuration.

- 16 -

- Uses controller software designed
- High frequency hardened for TIG welding (GTAW), plasma welding (PAW) and plasma cutting (PAC)

The rotary vector speed reducers, in the three major axes provide smoothness  
5 of motion at low speeds. Further, rotary vector speed reducers do not limit the  
stroke of the axis giving the robot 160 a large work envelope than robots with  
ballscrews. The standard sixth axis allows programming of optimum torch angles  
for faster, more efficient spraying including out-of-position locations. Floor, angle,  
and inverted mount configurations make it the robot 160 adaptable to many  
10 application layouts. The robot 16 has a stiff wrist due to few components with  
harmonic drives for quick and smooth operation.

Figure 9 illustrates a material handling system 22 which moves a pallet 180  
under a masking system 182 via a conveyor system 186. The pallet 180 has the  
substrates 184 to be coated with EMI/RFI shielding coatings mounted thereto. The  
15 material handling system 32 moves the substrates 184 through the system 10 of the  
present invention. A robot 160 including an HVOF thermal spray gun 18 mounted  
thereto, applies the coating in accordance with the method of the present invention.

A preferred embodiment of the mask 182 in accordance with the present  
invention includes electroformed nickel coated with nonstick material such as, for  
20 example, silicone. Crossbars 188 for masking holes and pins are included in the  
mask.

Referring to Figures 10 and 11, a view of the inside surfaces 200 of the back  
cover 202 of a wireless telephone that has been sprayed with the EMI/RFI shielding  
coatings in accordance with the present invention and an exploded view of a  
25 wireless telephone 210 using the EMI/RFI shielding coatings of the present  
invention respectively are illustrated. The EMI/RFI shielding coatings can be  
applied to surfaces of arbitrary orientation, for example vertical, horizontal or angled  
surfaces of a substrate including both exterior and internal sidewalls. The surfaces  
that are masked include, but are not limited to, holes, bosses, pins, cavities and  
30 edges. Further, surface tolerances such as, for example, flatness and internal

- 17 -

dimensions are maintained using the method in accordance with the present invention.

The EMI/RFI shield 214 that results from the system and method of the present invention has a high density level for maximum electrical conductivity and a high level of adhesion with minimum and preferably no delamination. No flaking off of minute particles results from the method of the present invention. The EMI/RFI shield has a good thickness uniformity (i.e. less than a 20% variation in thickness) and coverage, including around bosses, in deep covers, and along vertical walls of a substrate. The resultant substrate has a smooth surface and an appearance not marred by shading or roughness.

Figure 12 is a flow chart illustrating the method of application of the EMI/RFI shielding coatings, on substrates in accordance with the present invention. Per step 250, the process is started with a clean plastic part. The part may be cleaned, if necessary, with compressed gas or with some mechanical means such as, for example, a brush, etc. In the next step 252, the surface of the substrate is prepared for coating deposition. The surface may be flat and need no further preparation as in a preferred embodiment. In the alternative, the surface may have a texture or roughness imparted during the molding process. The surface may be precoated with a polymer or etchant to chemically react with the surface to create a rougher texture. Further, the surface may be coated with a self-bonding metal containing e.g. molybdenum or Ni-Al. In yet another embodiment, the surface may be abraded using abrasive media such as, but not limited to, aluminum oxide grit, glass beads or walnut shells.

The substrate parts are then masked for metal deposition per step 254. The part may be masked by one of several methods, such as, for example, with adhesive tape, or the part may be masked with various paint-on materials, or the part may have molded rubber, polymer or metal plugs and screws to serve as masks or part may be fitted with a formed metal or polymer mask. It should be noted that the method of the present invention does not require frequent mask changes or mask cleaning.

Per step 256, metal coatings are deposited. The coating is deposited by a high velocity oxy-fuel thermal sprayer with a metal feed. The coating is deposited by traversing the spray head over the part or by moving the substrate relative to the spray head. The HVOF sprayer achieves coatings on surfaces of a substrate with a minimum number of passes, such as for example, one or two passes because the deposition rate of the coatings is high and provides uniform coverage. The traverse rate of the spray head is at a high level which gives an increased level of throughput and a low level of substrate warping. The throughput is high because the gun moves at a high rate (200-1200 mm/sec) and does not have to stay over the parts for an extended duration. The sprayer moves from one pallet of substrates to another without being depowered. The deposition efficiency is an increased level than the prior art. The coatings may be any metal in wire form, but preferably, tin, zinc, aluminum, silver, copper, nickel, a metal-plastic composite wire or various alloys. The coating thickness may range from .0005" to typically several thousandths of an inch.

The part is then unmasked per step 258. The part is removed from the mask and plugs, screws, tape, etc. are removed. No post spray operation is required using the method of the present invention.

The adhesion of the HVOF sprayed coatings on Polycarbonate/Acrylonitrile-Butadiene-Styrene (PC/ABS) plastic lie in the range of about 650 to 1070 psi as measured by the standard ASTM method. These values are about three to ten times higher than the prior art arc wire sprayed coatings on the same substrate composition. The electrical conductivity of the HVOF sprayed coatings in accordance with the present invention is in the range of about 5 to 10 mohms/square cm. These conductivity levels are about two to four times lower than the prior art arc wire sprayed zinc coatings and about five to ten times better than the best conductive paints.

The HVOF sprayed coatings in accordance with the present invention can be sprayed on a variety of plastic materials. The classes of plastic materials that can be coated using the present invention includes, but is not limited to, styrenic molding

compounds, for example ABS, thermoplastic molding compounds, for example, polypropylene, and thermoset molding compounds, for example, polyimide.

It should also be noted that to minimize and preferably prevent heat distortion effects the parameters of the present invention are varied. The parameters  
5 that are varied include, but are not limited to, the fixture, cooling apparatus surrounding substrates such as, for example, circulating cooling water in the mounting fixture, or convectively cooling the substrates with air, traverse rate of the HVOF sprayer and deposition rate of the wire.

The system and method of applying EMI/RFI shielding coatings has several  
10 benefits. The application of the shielding coating with high velocity provides a high level of adhesion, an increased level of coverage on vertical surfaces without manipulating the sprayer, an increased level of density with low oxide content which results in an increased level of electrical conductivity as compared with the prior art. Further, the high velocity allows for the use of thinner coatings for a level of  
15 electrical conductivity, which translates to a more efficient process that involves less time to spray with less material. The high velocity also provides coverage in deep corners, cavities, and around bosses. A smooth, flake free surface results by using the present invention method. Additionally, the high velocity provides coatings with an increased level of particle cohesiveness which protects against the coating  
20 breaking apart if the surface of the substrate is bent.

There are several advantages of the EMI/RFI shielding coatings of the present invention over coatings that result from a painting process of the prior art. Metal coatings have no volatile organic compounds (VOC), while painting does. Thus painting causes lots of environmental problems. Further, paint requires drying  
25 and baking operations, while deposition using the system of the present invention, does not. Paint has much higher electrical resistance than metal and paint is more expensive than metal. Masking paint is harder because the paint sticks to the masks better so one must clean them more frequently. Cleaning requires immersion in solvents. Metal spray masks do not collect over spray so easily and can be cleaned  
30 with compressed air. Metals are easy to recycle, e.g. zinc and hydrochloric acid,

- 20 -

aluminum and sodium hydroxide. Paints are harder. Metals are easier to spray because, with their high particle velocities, they bounce around and coat vertical sidewalls. Paint requires more direct angles and therefore more robot articulation.

While this invention has been particularly shown and described with  
5 references to preferred embodiments thereof, it will be understood by those skilled in the art that various changes in form and details may be made therein without departing from the scope of the invention encompassed by the appended claims.

- 21 -

## CLAIMS

What is claimed is:

1. A system for applying a metal layer to a surface of a substrate comprising:  
a high velocity combustion sprayer positioned relative to a substrate  
5 support;  
a gas flow controller that provides a flow rate of a carrier gas and a  
fuel to the sprayer; and  
a metal source that delivers a metal to the sprayer such that the metal  
is sprayed onto a substrate.
- 10 2. The system of Claim 1 further comprising a material handling system that  
positions the substrate relative to the sprayer.
3. The system of Claim 1 further comprising a holding fixture including a robot  
that controls relative movement between the sprayer and the substrate.
4. The system of Claim 1 wherein the substrate is formed from at least one of  
15 plastic, metal and a composite of plastic and metal.
5. The system of Claim 1 wherein the metal layer comprises an EMI/RFI  
shielding layer.
6. The system of Claim 1 wherein the substrate comprises a telephone housing.
7. The system of Claim 1 wherein the sprayer accelerates metal particles to a  
20 speed of at least 330m/sec.
8. The system of Claim 1 further comprising a process controller connected to  
the sprayer.

- 22 -

9. The system of Claim 1 wherein the metal source includes a wire feeder that delivers wire into the sprayer at a controlled rate.
10. A high velocity thermal sprayer comprising:
  - a sprayer body;
  - 5 a nozzle assembly having an air cap having an inlet bore portion, and an outlet bore portion, a mixing plug, a supply of fuel for ignition in the nozzle assembly, a supply of air under pressure; and
  - a supply of feed stock that is delivered to the sprayer such that the feed stock melts and accelerates towards a surface of a substrate.
- 10 11. The high velocity oxy-fuel thermal sprayer of Claim 10 wherein the air cap has at least two ports for the introduction of air under pressure.
12. The high velocity oxy-fuel thermal sprayer of Claim 10 wherein the air cap has a second inlet for introducing air under pressure.
13. The high-velocity oxy-fuel thermal sprayer of Claim 10 further comprising a  
15 first sealing member disposed around an inner bore between the mixing plug and the nozzle and a second sealing member disposed around an outer bore between the mixing plug and the nozzle.
14. The high velocity oxy-fuel thermal sprayer of Claim 10 wherein the sprayer further comprises an igniter.
- 20 15. The high velocity oxy-fuel thermal sprayer of Claim 10 wherein the feedstock comprises a metal that forms melted particles that are accelerated to a speed of at least 330 m/sec. by the nozzle.

16. The high velocity oxy-fuel thermal sprayer of Claim 10 further comprising a gas flow controller that regulates gas flow into the sprayer.
17. The high velocity oxy-fuel thermal sprayer of Claim 10 further comprising a feeder that delivers the feedstock into the sprayer and a process controller  
5 connected to the sprayer.
18. A method fo spraying EMI/RFI shielding on a surface of a substrate comprising:
  - positioning the substrate with a surface in a holding fixture;
  - forming a spray of metal particles;
  - 10 directing the spray of metal particles towards the surface of the substrate with a speed of at least about 330 m/sec; and
  - forming a layer of EMI/RFI shielding on the substrate.
19. The method of Claim 18 wherein the step of forming a spray of molten metal includes heating oxygen having a gas flow rate of from 225 to 325 scfh and a  
15 fuel gas having a gas flow rate of from 25 to 45 scfh and flowing air under pressure having a gas flow rate of from 18 to 28 scfm.
20. The method of Claim 18 wherein the step of forming the spray of molten metal particles includes heating a metal wire feedstock having a feed rate of about 3 to 24 lb/hr.
- 20 21. The method of Claim 18 wherein the step of forming the spray of metal particles includes translating the HVOF thermal sprayer at a rate of about 200 to 1200 mm/sec.
22. The method of Claim 18 wherein the EMI/RFI shielding has an adhesion characteristic of about 650 to 1070 psi in tension.

- 24 -

23. The method of Claim 18 wherein the distance between the spray of molten metal particles and the surface of the substrate is in a range of about 4 to 12 inches.
24. The method of Claim 18 wherein the substrate is formed from at least one of plastic, metal and a composite of plastic.
25. The method of Claim 18 further comprising providing a telephone housing substrate.
26. The method of Claim 18 further comprising providing a zinc material that forms the spray of metal particles.
27. The method of Claim 18 further comprising providing a copper material that forms the spray of metal particles.
28. The method of Claim 18 further comprising providing an aluminum material that forms the spray of metal particles.
29. The method of Claim 18 further comprising spraying a metal alloy on the substrate.
30. The method of Claim 18 further comprising providing a substrate having a sidewall surface that extends at an angle relative to the substrate surface such that the layer extends uniformly across the substrate surface and the sidewall surface.
31. The method of Claim 18 further comprising controlling the spraying of the layer using a process controller connected to a sprayer.

- 25 -

32. A composite structure comprising a substrate and a metal layer having an adhesion characteristic of at least about 650 psi and an electrical conductivity level of at least about 5 mohms per square cm.
33. The composite structure of Claim 32 wherein the composite structure has an  
5 adhesion characteristic in the range of 650 to 1070 psi.
34. The composite structure of Claim 32 wherein the composite structure has an electrical conductivity level in the range of 5 to 10 mohms per square cm.
35. The composite structure of Claim 32 wherein the metal layer comprises an EMI/RFI shielding layer.
- 10 36. The composite structure of Claim 32 wherein the substrate comprises a plastic material.
37. The composite structure of Claim 32 wherein the substrate comprises a molded plastic telephone housing.
38. The composite structure of Claim 32 wherein the substrate has a first surface  
15 and a sidewall, the first surface and the sidewall being at an angle between 10° and 170° relative to each other.
39. The composite structure of Claim 38 wherein the metal layer extends uniformly along the first surface and the sidewall.
40. The composite structure of Claim 37 wherein the housing has a plurality of  
20 chambers and a plurality of sidewalls extending between the chambers such that the chambers are shielded from each other.

1/14

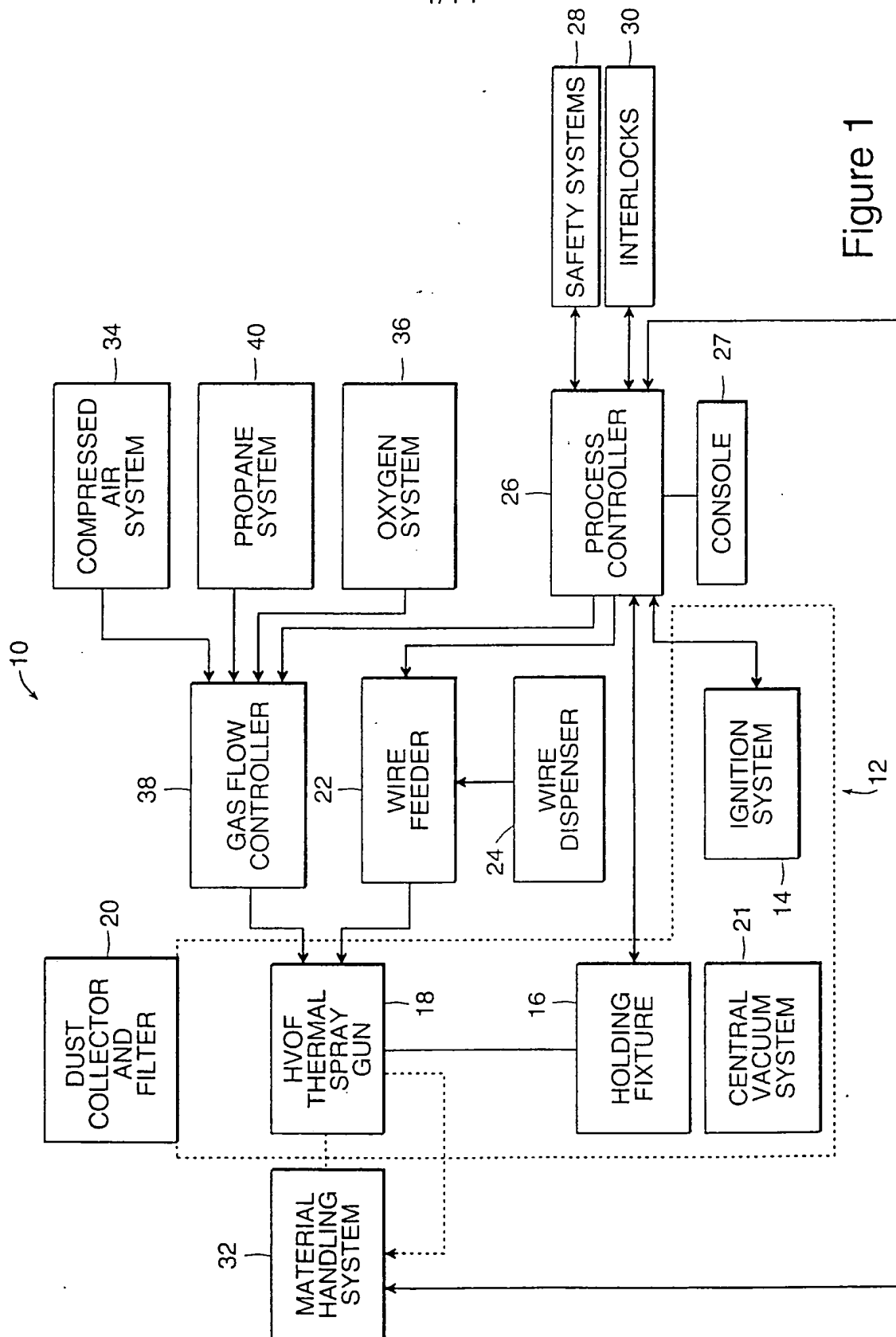


Figure 1

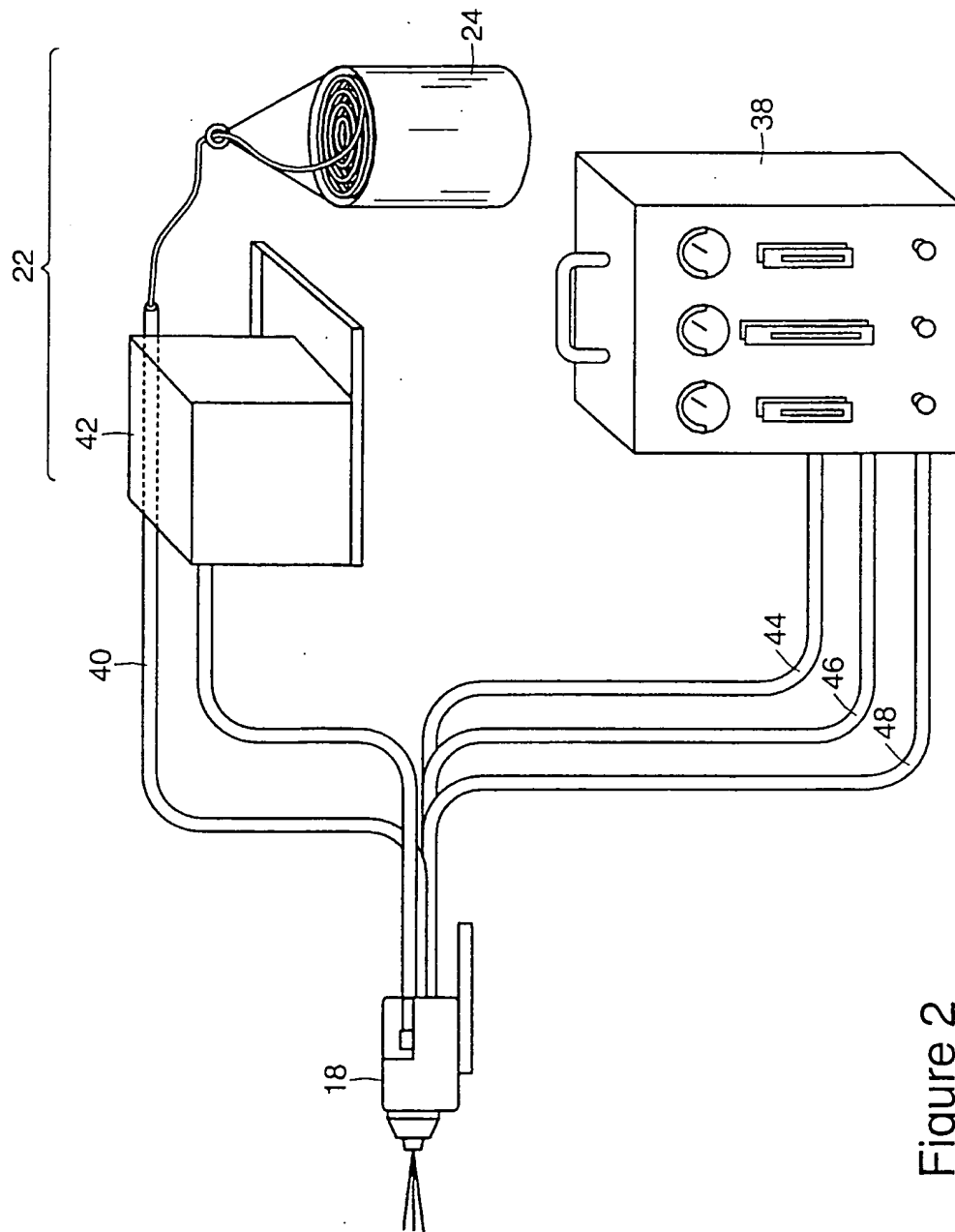


Figure 2

3/14

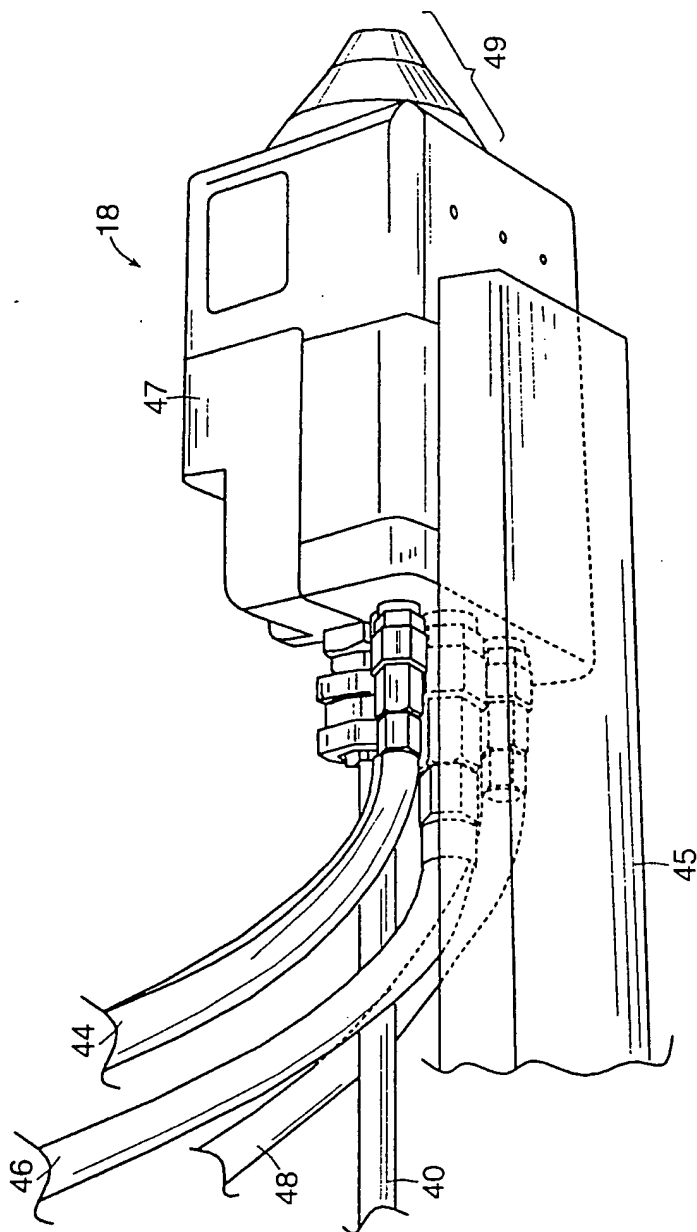


Figure 3A

4/14

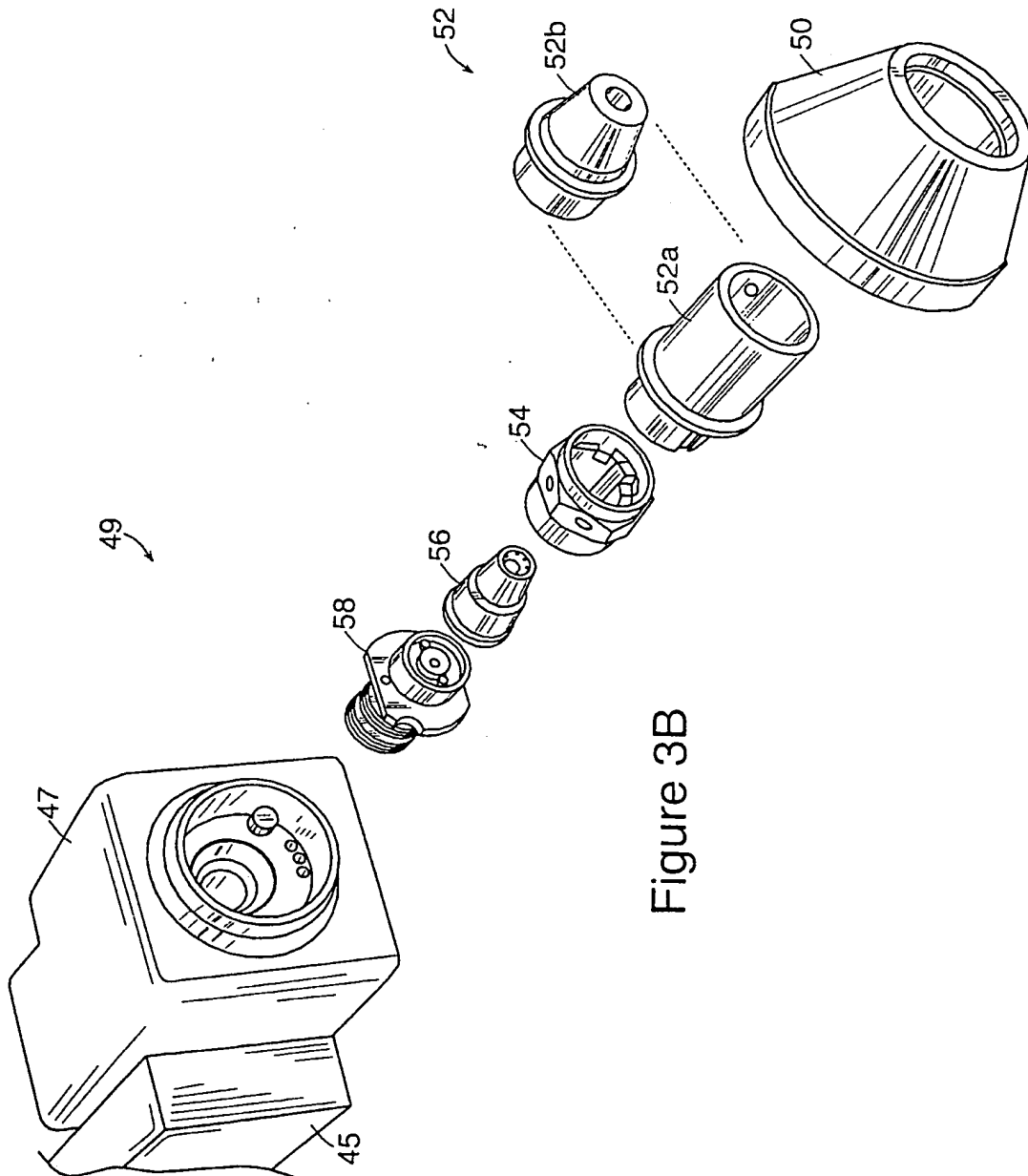


Figure 3B

5/14

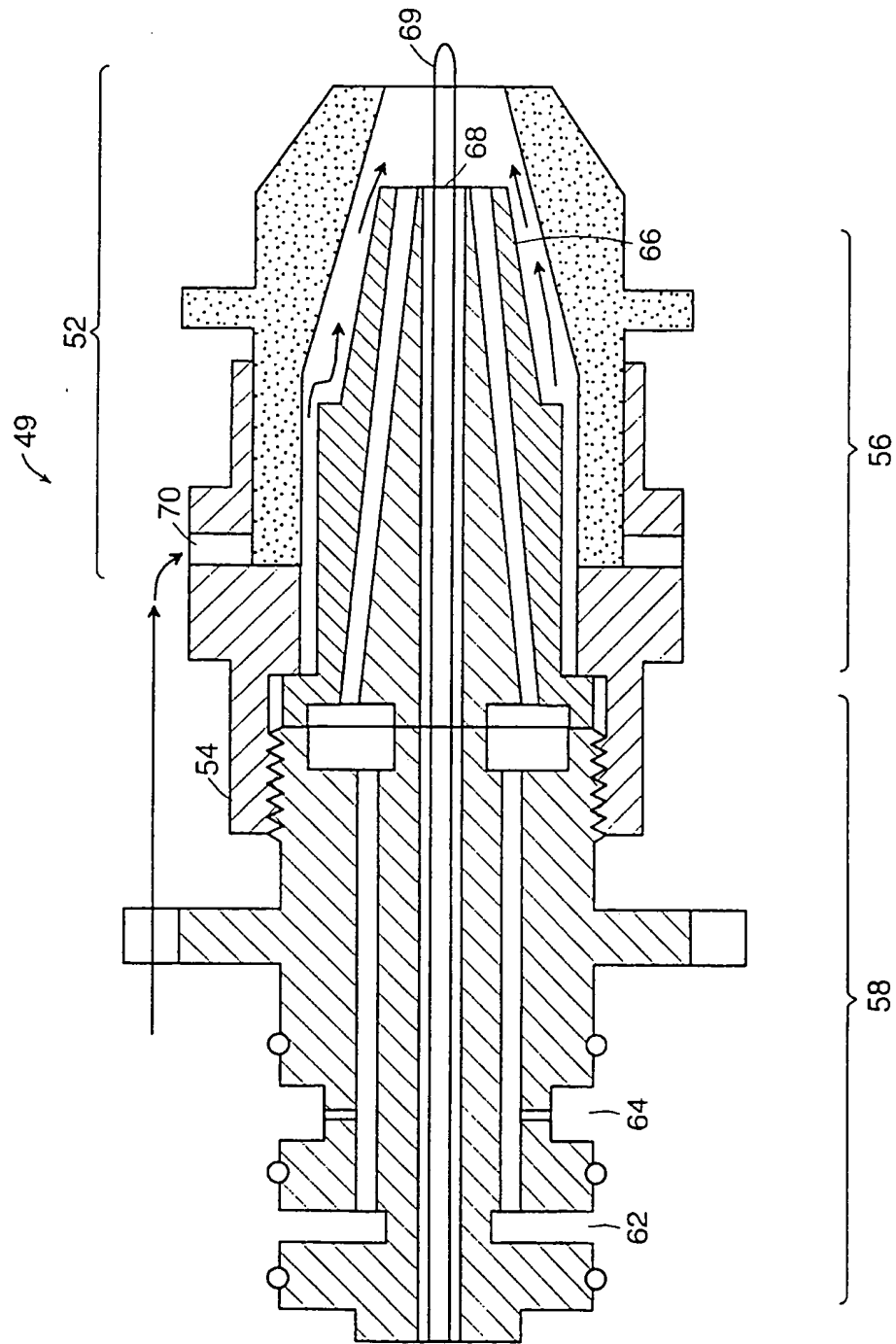


Figure 4

6/14

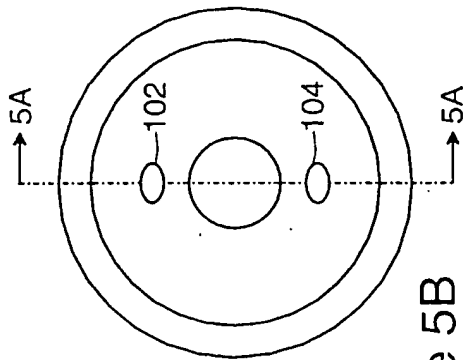


Figure 5B

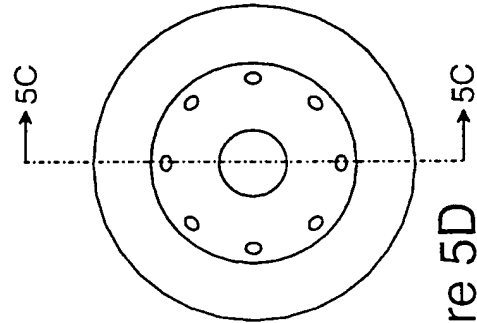


Figure 5D

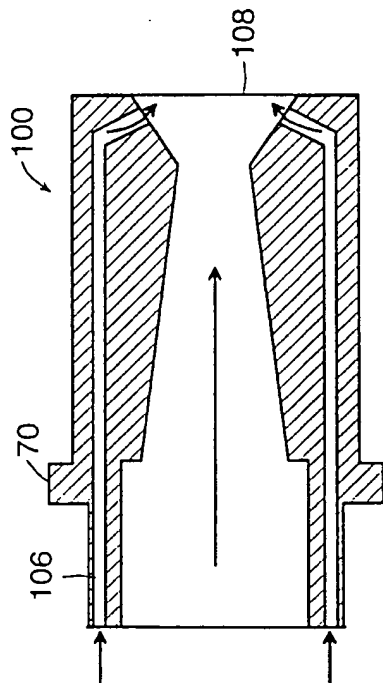


Figure 5A

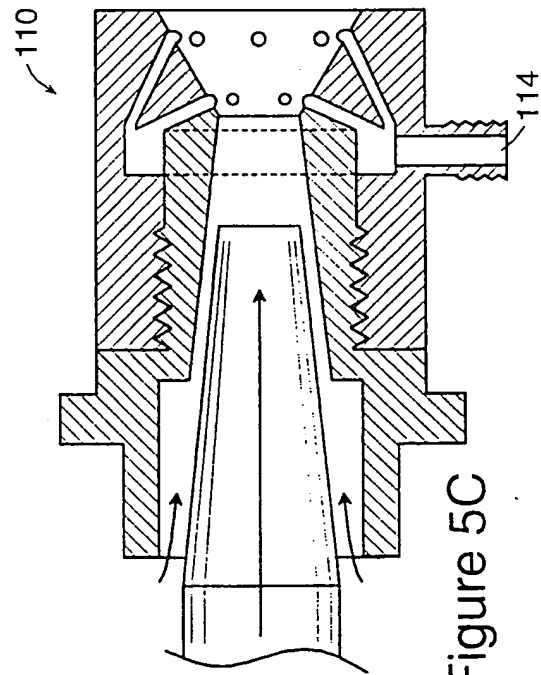


Figure 5C

7/14

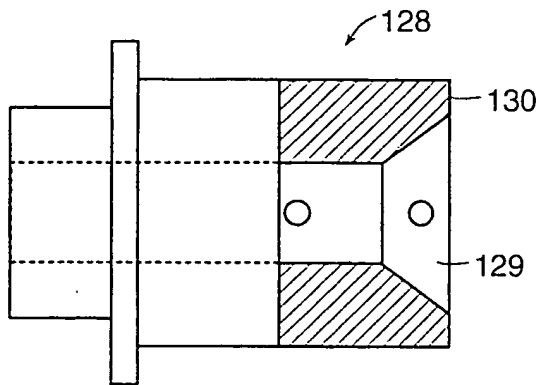


Figure 5E

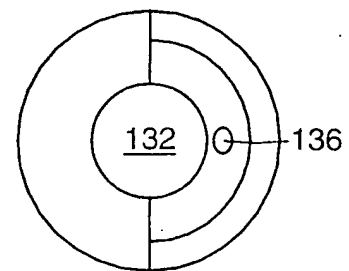


Figure 5F

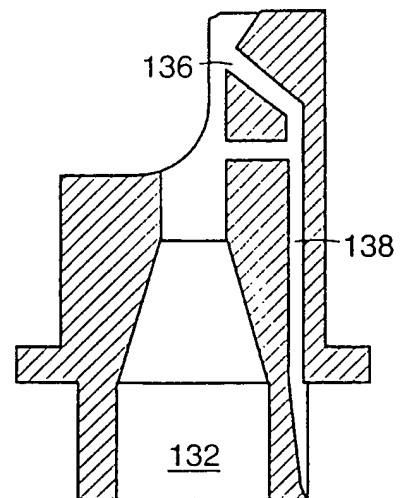
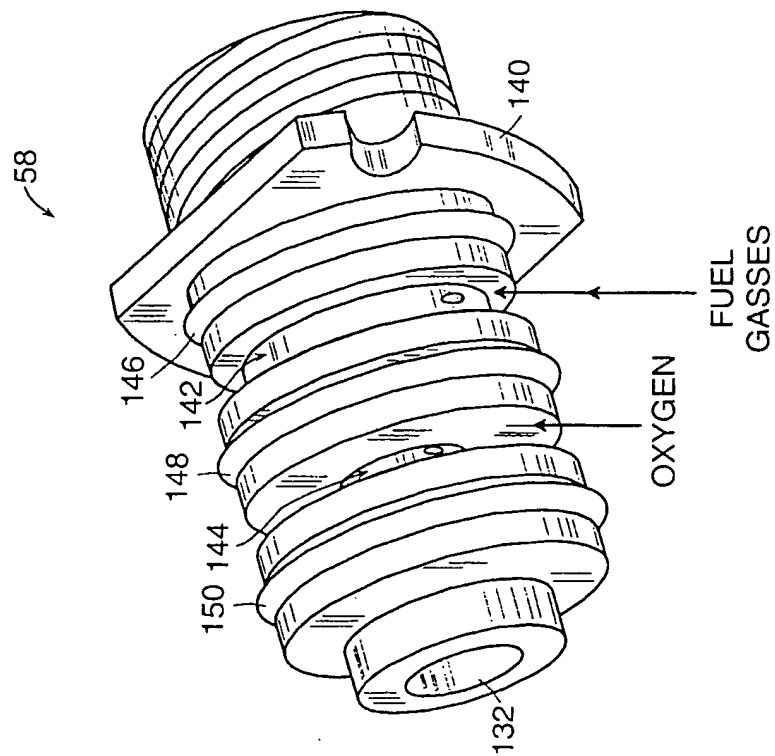


Figure 5G

8/14

Figure 6



9/14

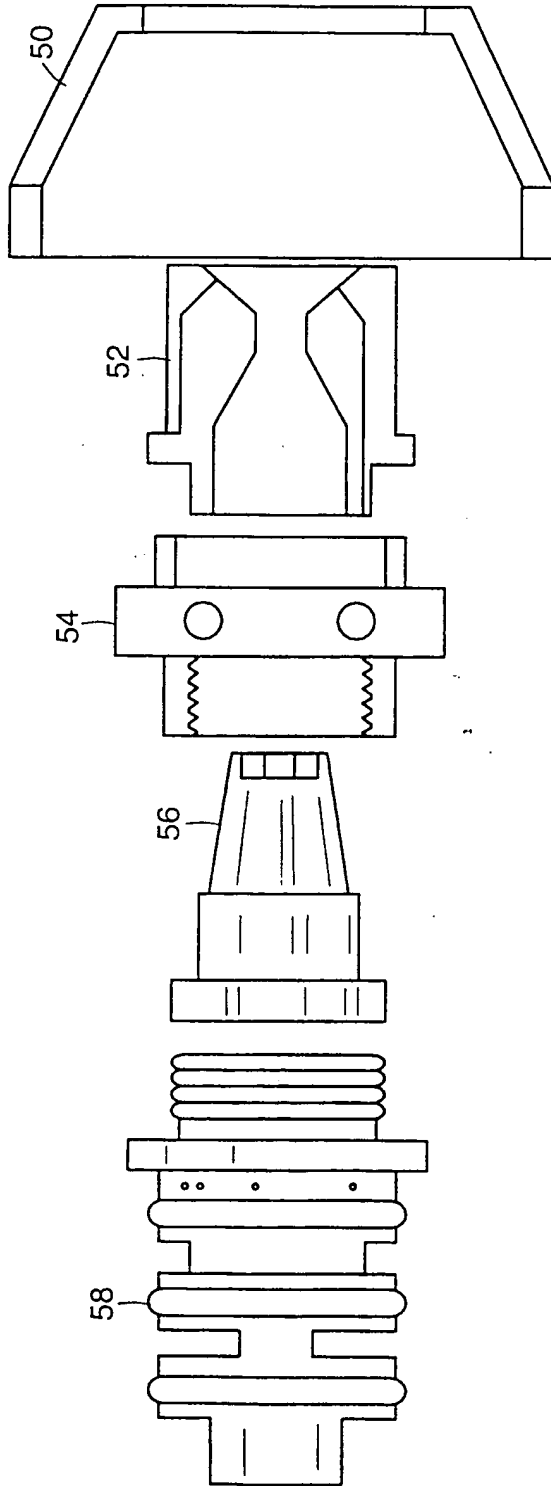


Figure 7A

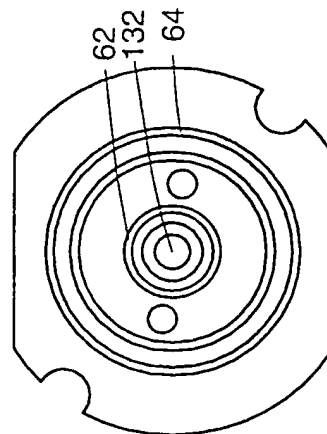


Figure 7B

10/14

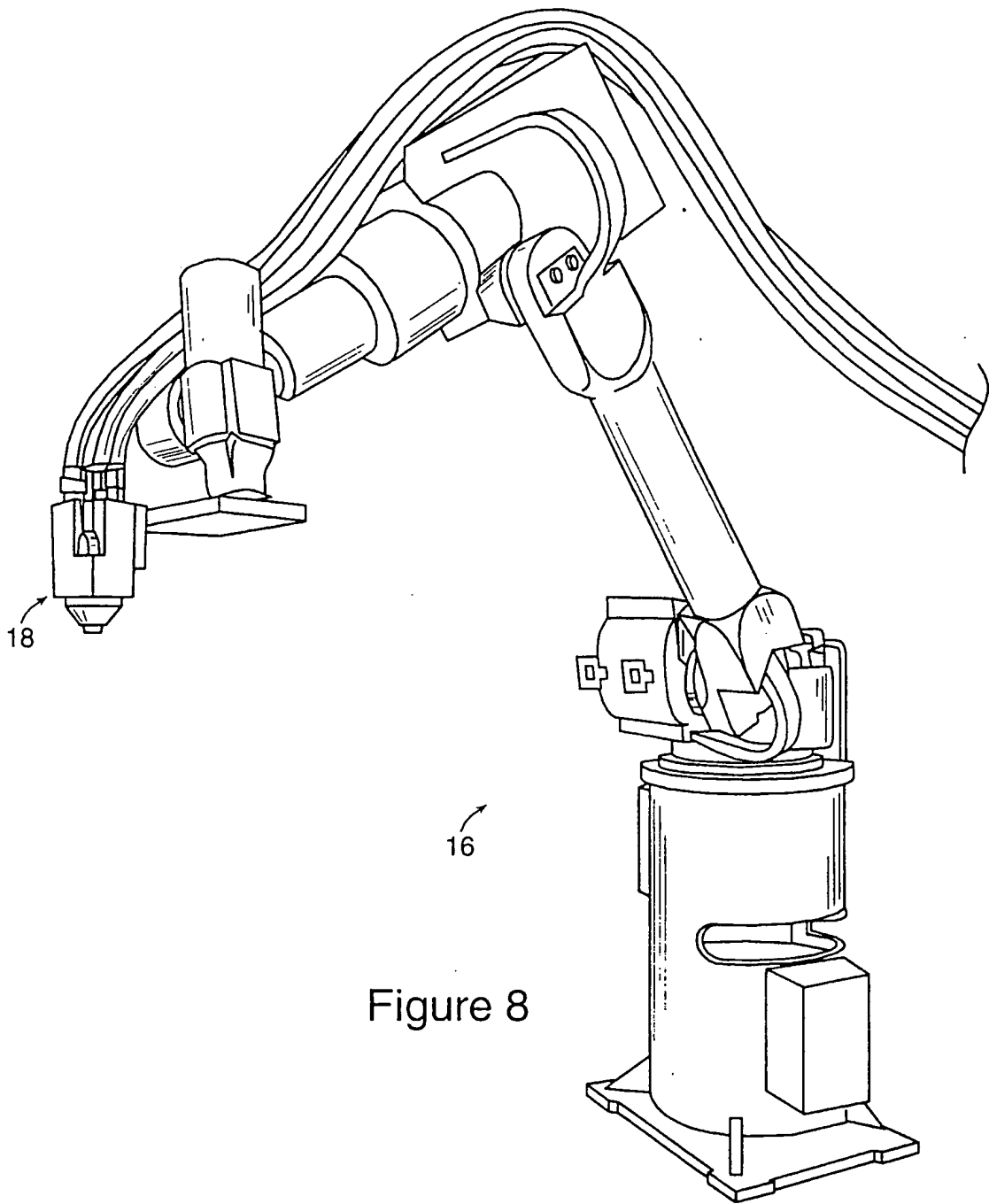


Figure 8

11/14

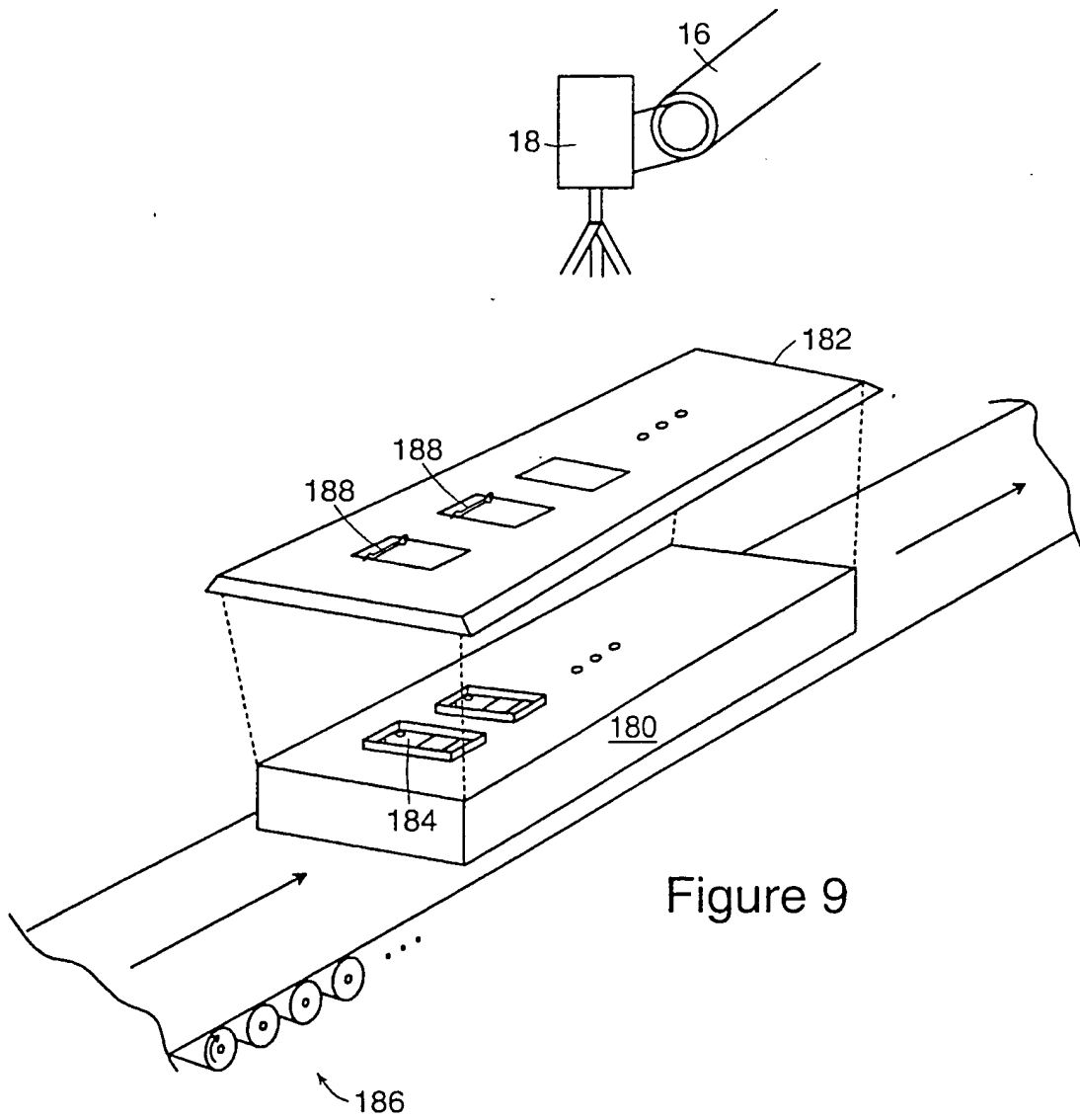


Figure 9

12/14

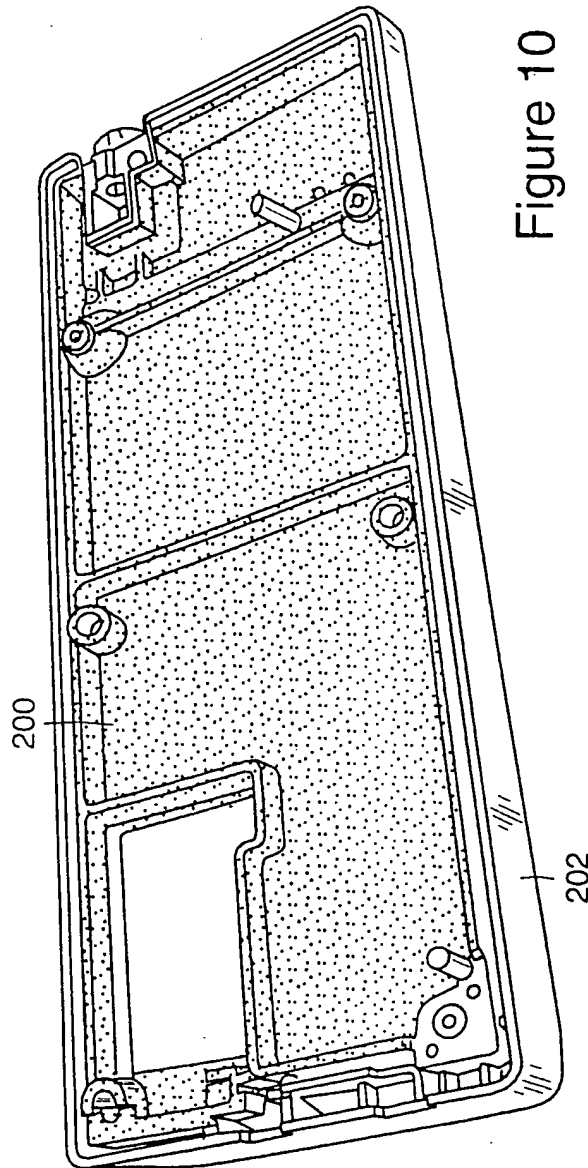


Figure 10

13/14

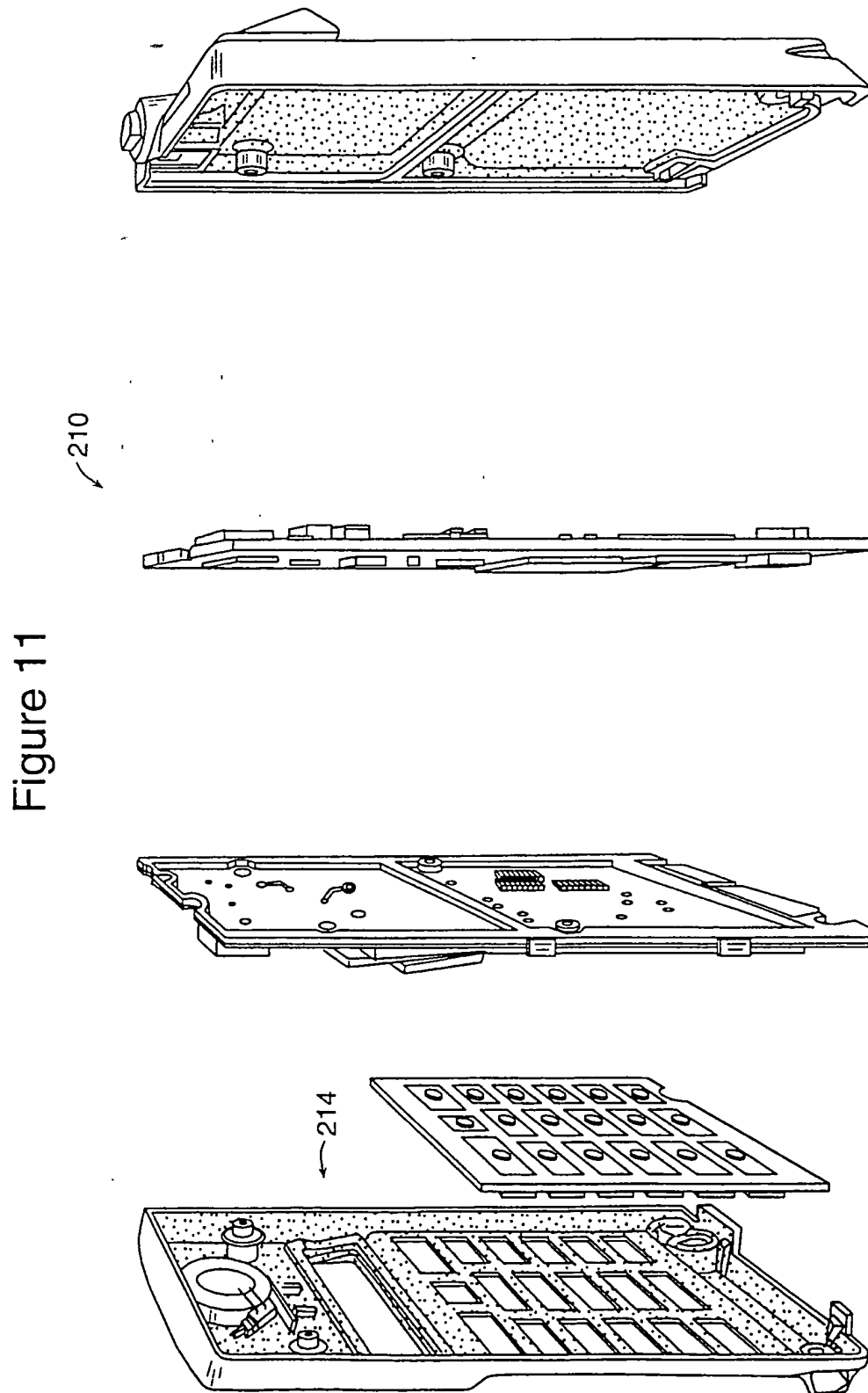


Figure 11

14/14

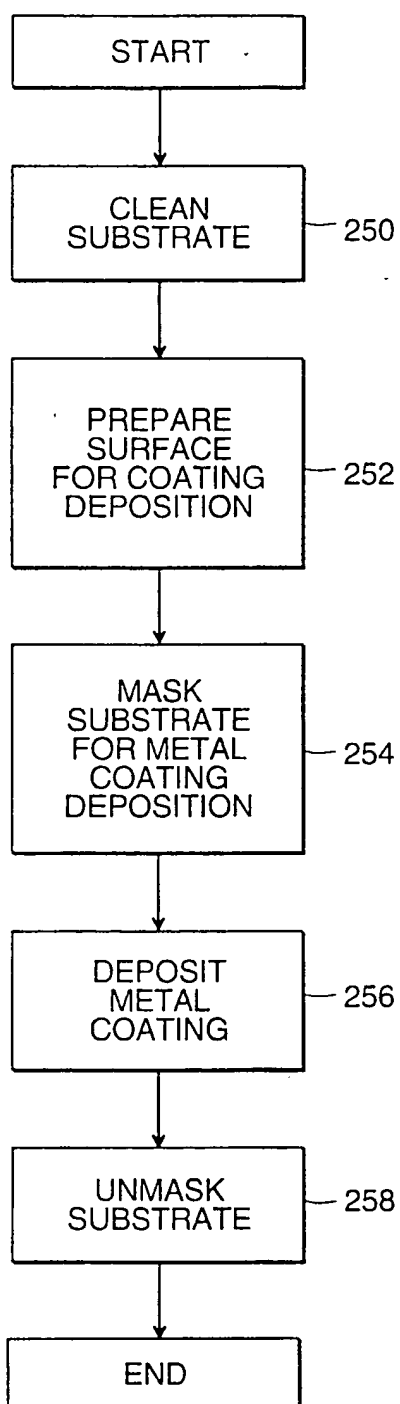


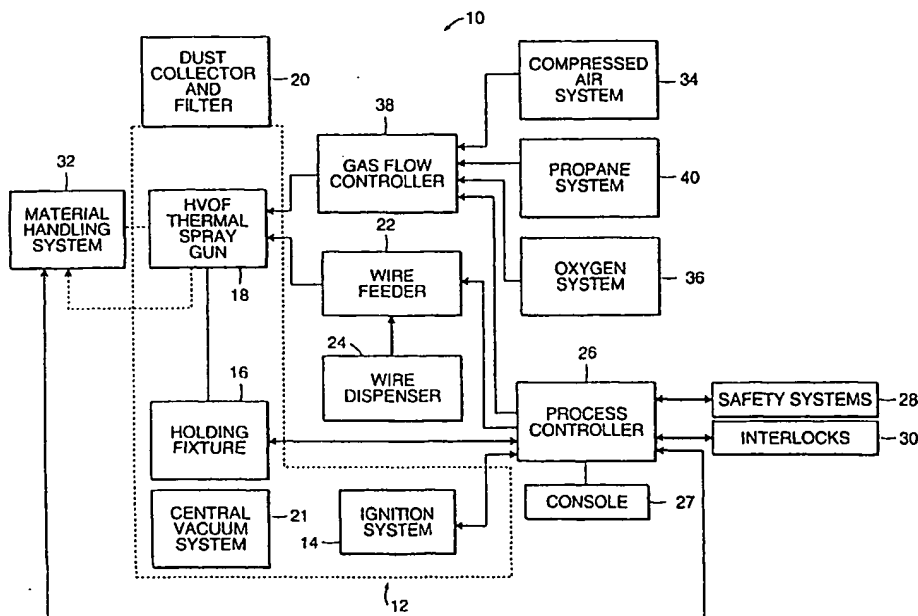
Figure 12



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>7</sup> : <b>C23C 4/12</b>		<b>A3</b>	(11) International Publication Number: <b>WO 00/29635</b>
			(43) International Publication Date: 25 May 2000 (25.05.00)
(21) International Application Number: PCT/US99/26634 (22) International Filing Date: 12 November 1999 (12.11.99) (30) Priority Data: 60/108,223           13 November 1998 (13.11.98)   US 60/162,577           29 October 1999 (29.10.99)   US (71) Applicant (for all designated States except US): THERMOCE- RAMIX, L.L.C. [US/US]; 101 Federal Street, Boston, MA 02110 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): ABBOTT, Richard, C. [US/US]; 68 Old Colonial Drive, Gardner, MA 01440 (US). COLLIER, Paul, S. [US/US]; 13 Pond Path, North Hampton, NH 03862 (US). GLENN, William, A. [US/US]; 107 Broadmeadow Road, Groton, MA 01450 (US). (74) Agents: HOOVER, Thomas, O. et al.; Hamilton, Brook, Smith & Reynolds, P.C., Two Militia Drive, Lexington, MA 02421 (US).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published With international search report. (88) Date of publication of the international search report: 8 September 2000 (08.09.00)	

(54) Title: SYSTEM AND METHOD FOR APPLYING A METAL LAYER TO A SUBSTRATE



## (57) Abstract

The present invention relates to systems and methods for applying metal shielding coatings on substrates. More particularly, EMI/RFI shielding coatings are applied using an HVOF thermal sprayer adapted to increase the velocity of the molten metal particles. The shielding coatings have an adhesion characteristic and electrical conductivity level that is an improvement over the prior art shielding coatings.

*FOR THE PURPOSES OF INFORMATION ONLY*

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon	KR	Republic of Korea	PL	Poland		
CN	China	KZ	Kazakstan	PT	Portugal		
CU	Cuba	LC	Saint Lucia	RO	Romania		
CZ	Czech Republic	LI	Liechtenstein	RU	Russian Federation		
DE	Germany	LK	Sri Lanka	SD	Sudan		
DK	Denmark	LR	Liberia	SE	Sweden		
EE	Estonia			SG	Singapore		

# INTERNATIONAL SEARCH REPORT

Int. Patent Application No  
PCT/US 99/26634

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C23C4/12

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 361 710 A (SULZER PLASMA TECHNIK) 4 April 1990 (1990-04-04) column 16 -column 19; figures 1,5	1,4,8,9 10
A	DE 38 43 436 A (LINDE) 28 June 1990 (1990-06-28) column 4, line 34 -column 5, line 30; figures 1-3	1,4,8
X	DE 19 44 428 A (METALLGESELLSCHAFT) 11 March 1971 (1971-03-11) claims 1-6; figures 1-8	1,9,10 14
A	DE 39 18 200 A (CASTOLIN) 6 December 1990 (1990-12-06) column 3, line 46 -column 6, line 55; claims 1-34; figures 1-8	1,4,10
X	---	---
	--- -/--	



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

### \* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*A\* document member of the same patent family

Date of the actual completion of the international search

15 May 2000

Date of mailing of the international search report

22/05/2000

Name and mailing address of the ISA  
European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Elsen, D

# INTERNATIONAL SEARCH REPORT

Int. Patent Application No  
PCT/US 99/26634

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 341 672 A (THE PERKIN-ELMER CORPORATION) 15 November 1989 (1989-11-15) claims 1-13; figures 1-7 ---	10,14
X	WO 97 36692 A (METALSPRAY) 9 October 1997 (1997-10-09) page 13, line 15 -page 17, line 35; figures 1,2 ---	10
A	DE 27 55 585 A (KLÖCKNER-HUMBOLDT-DEUTZ) 19 April 1979 (1979-04-19) claims 1-12; figures 1-9 ---	1,2
A	EP 0 007 207 A (TRW) 23 January 1980 (1980-01-23) claims 1-24; figures 1-11 ---	2
A	WO 98 17837 A (KK TOSHIBA) 30 April 1998 (1998-04-30) abstract; figure 1 ---	2,3
A	EP 0 517 191 A (LINDE) 9 December 1992 (1992-12-09) claim 1 ---	7,15,21
A	EP 0 484 533 A (INSTITUT TEORETICHESKOI I PRIKLADNOI MEKHANIKI SIBIRSKOGO OTDELENIA AK) 13 May 1992 (1992-05-13) claim 1; figures 1,5 ---	7,15,21
A	US 4 578 310 A (RAYMOND W. HATFIELD) 25 March 1986 (1986-03-25) column 1, line 5 - line 41 column 3, line 5 - line 19 ---	4-6
A	JACKMAN J L: "EMI SHIELDING TECHNIQUES FOR PLASTIC PACKAGING" ACM. PROCEEDINGS OF THE ANNUAL CONFERENCE, 1984, XP000892291 ---	4-6
A	DE 38 06 178 A (SIEMENS) 7 September 1989 (1989-09-07) column 1, line 61 -column 2, line 34; claims 1,2 -----	1

# INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. Application No

PCT/US 99/26634

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 361710 A	04-04-1990	US 5019686 A AT 96183 T AT 103343 T AU 4133589 A AU 4133689 A BR 8904694 A BR 8904695 A CA 1329064 A CN 1041545 A CN 1042951 A DE 68910072 D DE 68910072 T DE 68914074 D DE 68914074 T DK 461989 A DK 462089 A EP 0361709 A EP 0570084 A ES 2045458 T ES 2050811 T FI 894379 A FI 894380 A JP 2131160 A KR 9514072 B NO 893746 A NO 893748 A PT 91753 A,B PT 91754 A,B US 5206059 A US 5262206 A ZA 8906634 A ZA 8906635 A	28-05-1991 15-11-1993 15-04-1994 29-03-1990 29-03-1990 01-05-1990 01-05-1990 03-05-1994 25-04-1990 13-06-1990 25-11-1993 24-03-1994 28-04-1994 30-06-1994 21-03-1990 21-03-1990 04-04-1990 18-11-1993 16-01-1994 01-06-1994 21-03-1990 21-03-1990 18-05-1990 21-11-1995 21-03-1990 21-03-1990 30-03-1990 30-03-1990 27-04-1993 16-11-1993 30-05-1990 30-05-1990
DE 3843436 A	28-06-1990	EP 0381836 A PT 92691 A	16-08-1990 29-06-1990
DE 1944428 A	11-03-1971	NONE	
DE 3918200 A	06-12-1990	NONE	
EP 341672 A	15-11-1989	US 4865252 A BR 8902185 A CA 1313948 A CN 1038597 A,B DE 68903030 D DE 68903030 T JP 1317564 A JP 2783289 B KR 9613923 B	12-09-1989 02-01-1990 02-03-1993 10-01-1990 05-11-1992 18-02-1993 22-12-1989 06-08-1998 10-10-1996
WO 9736692 A	09-10-1997	US 5932293 A AU 2219897 A	03-08-1999 22-10-1997
DE 2755585 A	19-04-1979	NONE	
EP 7207 A	23-01-1980	US 4334495 A AU 534262 B AU 4845179 A	15-06-1982 12-01-1984 17-01-1980

# INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. Application No

PCT/US 99/26634

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 7207 A		CA 1123345 A DE 2967523 D EP 0077476 A IL 57529 A IL 64517 A JP 1431569 C JP 55015694 A JP 62040072 B US 4358471 A US 4411940 A	11-05-1982 07-11-1985 27-04-1983 31-03-1983 29-04-1988 24-03-1988 02-02-1980 26-08-1987 09-11-1982 25-10-1983
WO 9817837 A	30-04-1998	EP 0952237 A	27-10-1999
EP 517191 A	09-12-1992	DE 4118469 A AT 126833 T DE 59203342 D ES 2078589 T	10-12-1992 15-09-1995 28-09-1995 16-12-1995
EP 484533 A	13-05-1992	WO 9119016 A DE 69016433 D DE 69016433 T US 5302414 B US 5302414 A	12-12-1991 09-03-1995 20-07-1995 25-02-1997 12-04-1994
US 4578310 A	25-03-1986	CA 1263929 A DE 3624574 A JP 62070467 A	19-12-1989 12-02-1987 31-03-1987
DE 3806178 A	07-09-1989	NONE	